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CHARACTERIZATION OF POLLUTANTS EXITING COKE QUENCH TOWERS

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Part I - Apparent Problems and Tentative Solutions

I. INTRODUCTION

Coke Manufacturing[1]

There are two generally accepted methods for manufacturing the steel industry's requirements for coke; the beehive process (nonrecovery) and the by-product, or chemical recovery process.

Today the by-product process produces about ninety-nine (99) percent of all metallurgical coke and is the only one considered in this paper. Economic factors have changed the traditional by-product plant operation. Although coke oven gas still remains as a valuable by-product for internal use, the production of light oils, ammonium sulfate and sodium phenolate are not usually profitable.

In a by-product coke plant bituminous coal is heated, out of contact with air, to drive off the volatile components. The residue remaining in the ovens is coke; the volatile components are recovered and processed in the by-product plant to produce tar, light oils, and other materials of potential value, including coke oven gas. This process is accomplished in narrow, rectangular, silica brick ovens arranged side by side in groups called batteries. Each coke oven is typically 18 inches wide, 15 feet high, and 40 feet long. Heat is applied by burning gas in flues located between the walls of adjacent ovens. About forty (40) percent of the gas produced by the coking process is used to heat the coke ovens. The remaining gas is used as a fuel in other mill operations.

Coal is charged through holes into the tops of the ovens from hopper bottom cars which run on tracks over the top of the battery. During the sixteen to twenty-four hour coking period, the gases and volatile materials distilled from the coal pass into the collection main(s) which run the length of the battery. At the end of the coking period, the doors are removed from each end of an oven and a long arm pushes the incandescent coke into the quench car. The car then moves to the

(1) Superior numbers refer to similarly-numbered references at the end of this paper.

quenching tower where the coke is cooled by water sprays. The cooled coke is delivered to handling equipment for subsequent use as a basic raw material for the blast furnaces.

Coke plant wastewater sources [2]

By-product coke plants vary widely in size, extent and type of by-product recovery, and wastewater practices. Wastewaters in coking originate from three principal sources: coal moisture, water of decomposition, and process waters added during gas treatment and by-product recovery. The process waters are the largest fraction of the total wastewaters and typically account for 60-85% of the total flow, which may range from 120-310 gal/ton depending on the level of process water recycle. Six categories of wastes are normally identified:

- tar still wastewater
- waste ammonia liquor (WAL) from the primary cooler
- ammonia absorber and crystallizer blowdown
- final cooler wastewater blowdown
- light oil (benzol) plant wastewater
- gas desulfurizer and cyanide stripper wastewater

QUENCH TOWER OPERATION

Typically 10 to 15 tons of hot (2000+°F) coke are quenched by 4,000 to 6,000 gallons of quench water every 10 to 15 minutes; the quenching of each load takes 2 to 3 minutes. 1,000 to 1,500 gallons of water is evaporated and the balance flows to a settling basin for removal of coke fines. In a plant where tight control is maintained of all water uses all of the contaminated coke plant waste water is typically evaporated by the hot coke.

QUENCH TOWER EMISSIONS

Particulate emissions and especially particulates produced by evaporating contaminated quench water have not been well documented.[3] [4] [5] A widely used method of controlling quench tower particulate emissions is to install baffles at the base of the quench tower above the hot coke car. Only limited information [3] is available on the effectiveness of this method in abating large particulates and practically no information is available on the effectiveness of baffles in abating other types of particulate emissions. In addition to particulate matter, quench towers are a source of gaseous pollutants. The character, magnitude and relationship of air emissions with respect to the levels of quench water contamination are not well documented.

Purpose

Many difficulties which have interferred with past test efforts need to be minimized in order to determine the relative impact of "dirty" and "clean" quench water on quench tower emissions.

Many quench towers are short rectangular "boxes" with low irregular velocities with internal chambers. Fugitive emissions frequently escape through the tower walls. Since the geometry of the stack would affect the results it was decided to test on a tall round stack (See Fig. 1), and further it was decided to test with both "clean" and "dirty" water in the same tower thus allowing differences caused by the makeup of the two types of quench water to be clearly indicated.

Work Plan

The following parameters are measured:

Ambient temperature and relative humidity outside the tower
Velocity profile across the cross sectional area of the tower at (10)
Particulate loading at (10)
Ambient air entering tower
Size distribution and composition of particulates and condensibles at (10)
Quench water quantity and composition
Return water quantity and composition
Temperature of incandescent and quenched coke
Gaseous emissions
Quenched and incandescent coke composition

Laboratory analysis of samples collected are in accordance with published EPA methods. Water samples are analyzed for:

Polycyclic Organic Matter (POM)	Calcium	Sulfide
Electrical Conductivity	BOD_5day	Sulfate
Total Organic Carbon	Phenols	Oils
Dissolved Solids	Ammonia	COD
Chlorides	Cyanide	pH

In addition, the exhaust gases are considered from the point of view of gaseous emissions and particulate emissions.

II. APPARENT PROBLEMS AND SOLUTIONS

Quench Tower Parameters	Apparent Problems	Tentative Solutions
1. Hostile environment, i.e. drizzle, grit and fumes.	Expect detrimental effect on humans and equipment - could affect ability to take reliable data	Provide protection select equipment with conditions in mind - Provide working and laboratory space close to test site.

2. Size and shape of stack, car doorway, configuration of nozzles.	Expect low velocity, cyclonic or skewed flow, uneven flow distribution across tower cross section, there will be fugitive emissions.	Traverse the area as Modified EPA Method 1 taking maximum number measurements. Determine angle of flow with Fecheimer probe, record extent of fugitive emissions and test when fugitives are minimal.
3. Short period of quench (2 to 3 minutes).	Sample volume for any one quench is limited and probably one quench will not provide a usable size sample.	High sample rates. Composite sample of several quenches.
4. Velocity, temperature, and moisture content vary with time during each quench period.	Isokinetic sampling rate is effected by all three of these factors and will therefore be variable with time during quench.	Estimate moisture, determine velocity and temperature profiles for each point prior to sampling and continuously record and adjust sampling rate.
5. Dew point temperature of stack gases above ambient temperatures, condensed steam (fog) and water droplets entrained in stack gases.	Sample lines outside stack and filter on sampling train will quickly plug with condensed water.	Remove most of the droplets by a calibrated cyclone on probe in the stack and/or heat the sample lines above the dew point.
6. Coke car may not be in exact same spot nor evenly loaded each time. Spray nozzles may plug or be otherwise non-uniform in distributing quench water.	Velocity profile may be quite different at any given point with different quenches.	Compare test results of sets of quenches at the same point to determine extent of variation; note car location and any abnormal spray operation.
7. Solid matter present as particles, or suspended in water droplets; dissolved solids.	Difficult to get a truly representative sample. Sampling method may not collect a given form or its form may be altered.	Use cyclones designed for specific cut sizes to sample particulate in the stack. Size the particles by appropriate analytical techniques.

8. Coke quality may vary from oven to oven and/or from battery to battery.	Physical and chemical parameters of one car may be different from another.	Observe and note "greens", note length of coking time and oven temperatures.

III. SUMMARY OF PARTICULATE SAMPLING TECHNIQUES BASED ON THE ABOVE SOLUTIONS

For the hi-volume mass concentration determination, a sampling apparatus devised at the Industrial Environmental Research Laboratory of the Environmental Protection Agency be used. Developed as a high volume sampling train for particulate measurement of stationary sources, it samples at a substantially higher flow rate than typical equipment, but follows the same procedures as outlined in EPA Method 5. (See Figure II)

This train has been modified with a cyclone precleaner (10 micron cut size) placed in the stack to separate out larger particles and remove some of the limited droplets.

A Hastings velocity meter was calibrated with special 10' probes. It was expected that the continuous purging of the pitot tubes would prevent plugging from condensed water or particulates.

Partially cleaned gases are drawn through a heated probe at about 4 cfm to a heated (250°F) filter where the balance of dry particulate matter is collected. The gas sample then passes through a cooler, a moisture knockout and a POM adsorber developed by Battelle.[6] Then the sample air passes through a typical impinger-silica gel train where condensible materials are removed and the gases are further dried prior to entering the flow control module.

Particulate collected by the knockout cyclone is analysed, dried and its weight added to the weight of dry material collected in the filter.

The following describes the functions and duties of the various test stations:

<u>Pump House Roof</u>

Records oven and battery number announces car approaching, car in, water on, water off, car out to Stack and Control center, signals Sump to start and end water sampling.

<u>Sump</u>

Obtains water samples at inlet, return and liquor lines, additional duties include assisting laboratory technician.

<u>Stack</u>

Operation of; EPA Method 5 Hi-Vol train(s), Hasting velocity meter(s), gas sampling trains, Orsat sampling and wet bulb-dry bulb testing.

Laboratory

Performs EPA Method 5 and gas sampling, set-up and clean-up procedures. Preserves and labels all water samples.

Control Center

Final authorization for start and end of all testing.

Performs conversion of velocity profiles to sampling rates and makes necessary changes due to varying conditions.

Records the following: velocity profiles of each Method 5 sampling train; phase distribution of plume temperature by the use of six (6) thermocouples located on the vertical plane of the stack; return and sump water temperatures.

VELOCITY PROFILE SEQUENCE (See Figure III)

Pump House reports car approaching; Stack and Control in ready position* announces car in, Control switches velocity recorder(s) on, water-on, profile continues, water off and car out, profile ends.

A minimum of two (2) cars are recorded to verify readings.

After verification, a sampling rate is determined along with the required nozzle size and given to the stack crew.

TEST SEQUENCE

Authorization for a test is given to both Stack and Pump House by Control. As the next coke car approaches the Pump House takes over and communicates all necessary sequences to Stack and Control Center.

With the command car-on the EPA Method 5 trains are switched on and the thirty (30) second ramp up to the selected sampling rate begins; when reached it is maintained until the water-off command is given and then a thirty (30) to forty (40) second ramp down is performed to a predetermined sampling rate.

After four (4) cars are tested the entire probe, cyclone, filter and impinger train are sent to the Laboratory trailer for breakdown.

During the test period the Pump House instructs the Sump to begin collecting composite samples of the inlet, return and liquor lines. These are then moved to the laboratory for preservation, labeling, and shipment along with gas and Method 5 samples to York Research for analysis.

* Probe located at desired position and angle in stack.

CONCLUSIONS

Preliminary results indicate most of the problems anticipated in testing emissions of a coke quench tower have been resolved or minimized through use of a high volume sampling rate, in-stack cyclones to knockout most of the mechanically entrained moisture, a warm dry air purge of the pitot tube, immediate interpretation of recorded velocity profiles, and concurrent calculation of flow rate settings.

ACKNOWLEDGEMENT

The authors acknowledge the advice of R. V. Hendricks and R. M. Statnick of the Environmental Protection Agency. Work supported by U.S. EPA Office of Enforcement under Contract 68-01-3161 and Industrial Environmental Research Laboratory (IERL) under Contract 68-02-1401.

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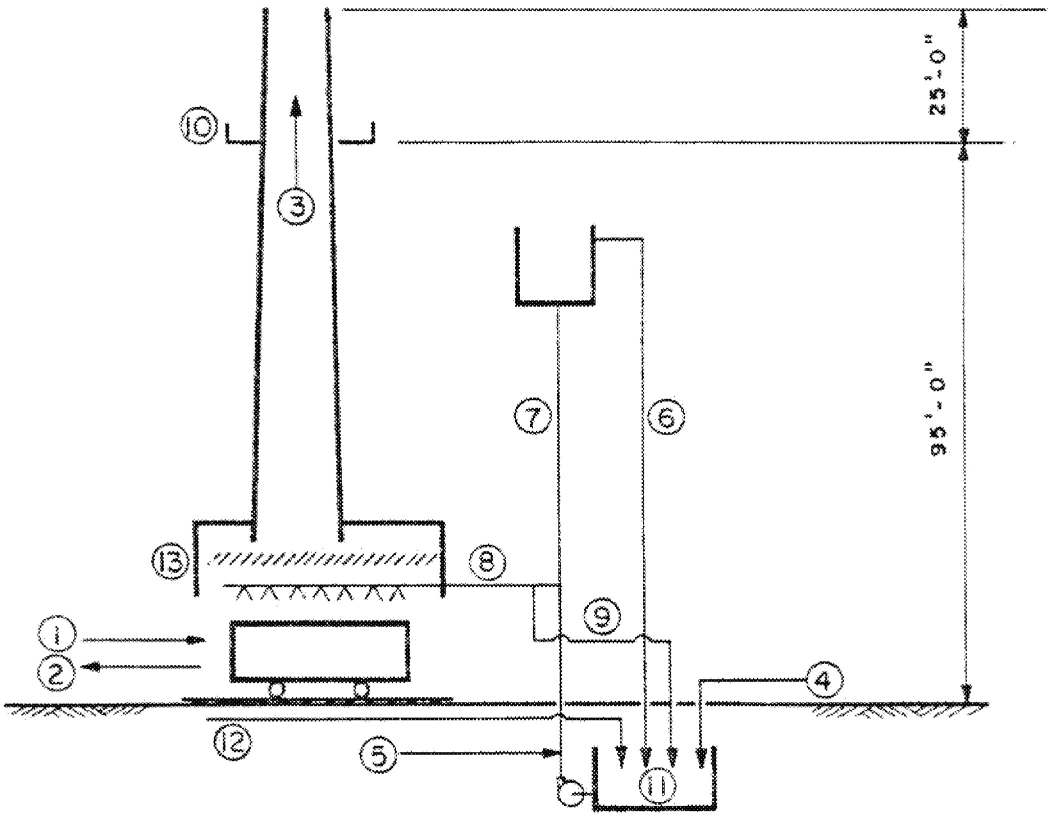
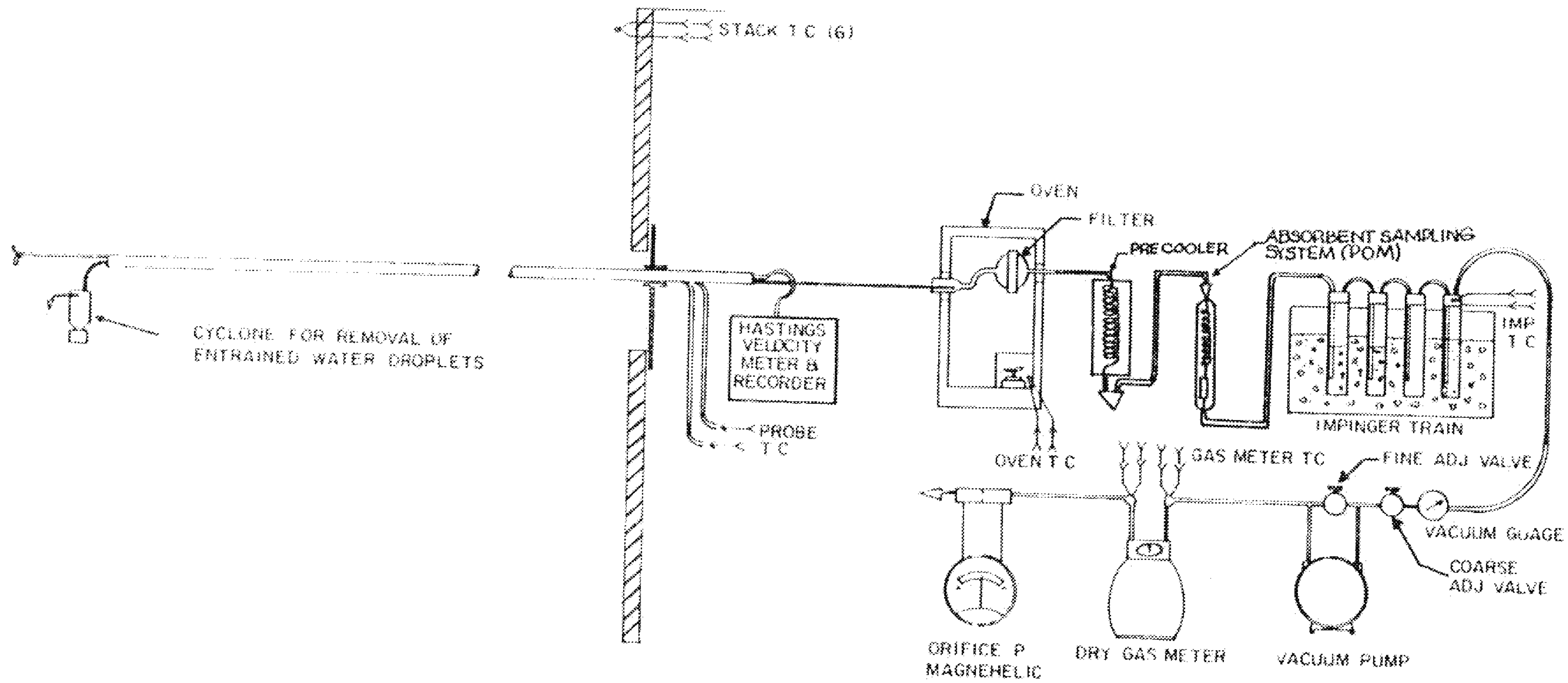


① INCANDESCENT COKE
② QUENCHED COKE
③ EXHAUST GASES
④ CONTAMINATED WATER
⑤ SERVICE WATER
⑥ HEAD TANK - OVERFLOW
⑦ HEAD TANK - STAND PIPE
⑧ NOZZLE HEADER
⑨ NOZZLE HEADER DRAIN
⑩ EMISSIONS TESTING STATION
⑪ SUMP
⑫ RETURN DRAIN DITCH
⑬ BAFFLES

Quench Tower

Figure I



MODIFIED SAMPLING TRAIN FOR
EPA METHOD #5
FIGURE II

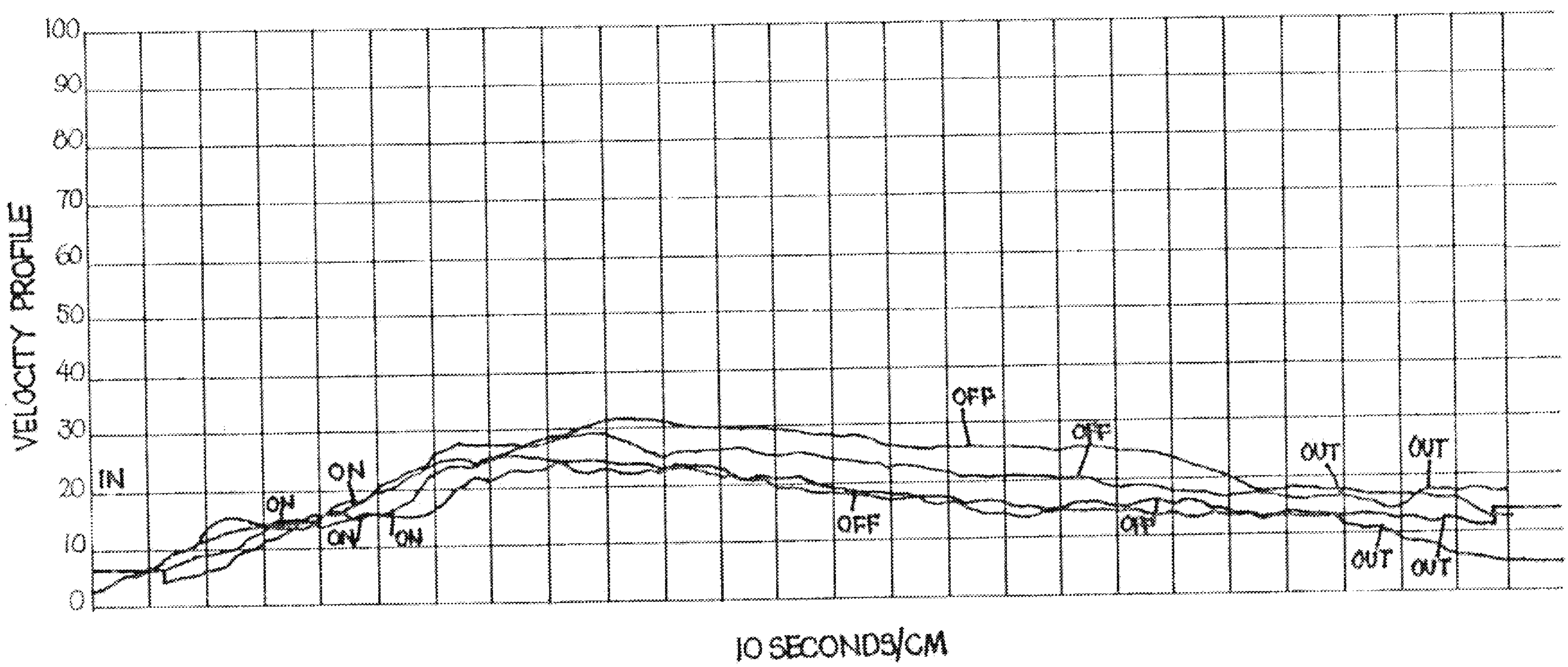

VELOCITY PROFILE
100
90
80
70
60
50
40
30
20
10
0
IN
ON
ON
ON
ON
OFF
OFF
OFF
OFF
OUT
OUT
OUT
OUT
10 SECONDS/CM

FIGURE III